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Sol-Gel Approaches for Solid Electrolytes and Electrode Materials

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Sol-Gel Approaches for Solid Electrolytes and Electrode Materials

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ABSTRACT

Sol-gel chemistry has a great many potential applications in the preparation of unique electrochemical materials, from non-equilibrium transition metal oxides which may be of use as high energy density electrodes, to high surface area mixed oxides which may possess high proton conductivity, to novel composite structures consisting of inorganic gels in combination with organic electronic and ionic conductors. This paper reviews prior work on proton conduction in gel systems and presents recent work regarding electrode materials prepared by sol-gel methods and inorganic-organic materials.

1. INTRODUCTION

The sol-gel process is a chemical synthesis technique for preparing gels, glasses and ceramic powders. It is based on the polymerization of molecular precursors via wet chemical methods. The sol-gel approach possesses a number of desirable features for solid state ionics. It enables one to prepare compounds at far lower temperatures than is possible by using conventional methods. Moreover, glass compositions which are difficult to obtain because of volatilization, high melting temperatures or crystallization problems can be produced. In addition, the sol-gel method is a high purity process which leads to excellent homogeneity.

The present paper considers the sol-gel process in a somewhat different context than simply the ability to synthesize oxide compounds and glasses. By controlling the chemistry of the process, one can prepare oxides in a variety of forms (powders, films, fibers, bulk monoliths) with tailored microstructures; from fully dense materials to highly porous, high surface area aerogels with < 1% solids. In this way sol-gel approaches provide some extremely interesting morphologies for electrochemical materials where the properties of surfaces and interfaces – and not the bulk – dominate the electrochemical behavior. This presents the possibilities of creating electrolytes in which surface conduction prevails and high rate electrodes that store charge by rapid intercalation reactions over small dimensions.

This paper begins with a brief overview of sol-gel chemistry and identifies selected areas where sol-gel synthetic approaches are likely to make contributions to solid state ionics. Rather than review older work concerning the use of sol-gel methods to prepare powders of solid electrolytes or cathode materials, we emphasize the use of the sol-gel process to produce new materials with controlled chemistry and morphology.

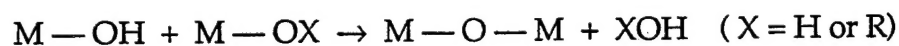
2. OVERVIEW OF SOL-GEL CHEMISTRY

The sol-gel technique enables one to prepare a wide variety of oxide materials. In this approach, metal-alkoxides, (formula $M(OR)_n$, where M is Al, Si, Ti, V, Cr, Mo, W, etc.... and R is an organic group) undergo hydrolysis followed by polycondensation reactions in solution at room temperature. The synthesis of oxides by this approach has been the subject of several reviews.¹⁻³

The sol-gel process can generally be divided into the following stages: forming a solution, gelation, drying and densification. The key feature in this sequence is sol-gel polymerization which can be described as a two-step reaction.⁴ Initiation is performed via the hydrolysis of alkoxy ligands. This leads to the formation of hydroxylated M-OH groups:



Propagation then occurs by the polycondensation of these hydroxylated species giving rise to oxypolymers. Polycondensation involves an oxylation reaction which, in turn, leads to the formation of oxygen bridges and the removal of XOH species as follows:

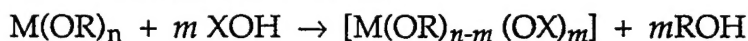


The chemical reactivity of metal alkoxides $M(OR)_n$ towards hydrolysis and condensation depends mainly on both the electrophilicity of the metal atom and its ability to undergo an increase in coordination number.⁴ Silicon alkoxide $Si(OR)_4$ precursors have a low electrophilicity and their coordination number is stable. Thus, the hydrolysis of $Si(OR)_4$ is slow and their polymerization reactions are mainly controlled by the use of acid or base catalysis.

The conditions under which the hydrolysis and condensation of silicates occur have a profound affect on gel morphology.² It is well appreciated that one can produce linear polymers, branched clusters or colloids in the solution depending upon various factors including the $H_2O:Si$ ratio and pH. Silicate gels prepared at low pH (< 3) and low water content (< 4 mol water per mol of alkoxide) produce primarily linear polymers with low crosslink density. Additional crosslinks form during gelation and the polymer chains become increasingly entangled. Silicate gels prepared under more basic conditions (pH 5-7) and/or high water contents produce more highly branched clusters which behave as discrete species. Gelation then occurs by linking clusters together.

The sol-gel chemistry of transition metal alkoxides is more complicated.⁴ Metal atoms not only have a high electrophilicity they can also exhibit several coordination states. Most alkoxides are highly reactive and precipitation occurs as soon as water is added. Thus, the synthesis of polymeric transition metal oxide based sols and gels requires careful control of the chemistry. Water used in

the hydrolysis of alkoxides can be diluted in solvent or provided *in-situ* via a chemical reaction. Another approach is to design molecular precursors via chemical modification prior to their hydrolysis.⁵ Since transition metal alkoxides react with nucleophilic reagents, they can be modified by using complexing ligands HOX (OX = acetylacetone, acetate):⁶



In this case the alkoxy groups (OR) are replaced by new ligands (OX) that are less easily removed upon hydrolysis. Thus, the alkoxy ligands are rather quickly removed upon hydrolysis while chelating ligands act as termination agents that limit condensation reactions.⁷

An important variation to the sol-gel process is the use of organic constituents to modify the oxide polymer developed from the alkoxide precursor. These materials, termed ORMOCERs (organic modified ceramics) or CERAMERs (ceramic polymers), are part of a rapidly expanding field where the final material is a molecular level composite consisting of an inorganic network in intimate contact with the organic component, frequently a polymer.⁸ The organic network can be linked to the inorganic backbone or act as an interpenetrating network. The interest in such inorganic-organic polymeric materials is that with the large number of chemical and structural modifications available, it is possible to design specific properties and produce novel materials with both inorganic and organic characteristics.⁹ A convenient method of incorporating organic groupings into an inorganic network is to bind non-hydrolyzable organic ligands to the molecular precursor. This approach has been particularly well developed for silicate systems. Recently, the synthesis of ORMOCERs containing transition metal oxides has been reported. The use of vanadate gels in combination with either conducting polymers or insulating polymers has been reported.^{10,11}

3. PROTON CONDUCTION

It is not surprising that sol-gel derived materials exhibit good proton conducting characteristics. From a chemical viewpoint, oxide gels may be considered to be hydrous oxides $MO_x \cdot nH_2O$. Water molecules are trapped within the oxide network and fully hydroxylated surfaces are developed. The colloidal particles are quite small and, therefore, the interfacial properties are very significant in determining transport properties. As a result, oxide gels have rather high conductivity for protons. Proton conduction mechanisms for a wide

range of solids including solid electrolytes and gels have been reviewed.¹² Gels are characterized by a "quasi-liquid" state on their surfaces and rather high proton conductivities are possible. Proton conduction at the surface of oxide particles also depends upon the relative humidity and this property has been applied in the development of humidity sensors.¹³

Silicate systems have an additional factor which can augment their proton conduction characteristics; the acid catalyst used in the synthesis provides a source of protons. At $\text{pH} < 4$, silicate sols exhibit conductivities comparable to those of the corresponding aqueous solutions.¹⁴ In the range $\text{pH} 4-7$, some variations from these values are observed and, interestingly, the conductivities of the sols are actually somewhat larger than those of the reference aqueous solutions. Upon gelation, there is relatively little change in conductivity as the solvent phase remains continuous. The measured resistance before and after gelation is shown in Figure 1. It is evident that there is no significant change in resistance during this time. The absence of any change in transport properties as the sol-to-gel transition occurs has also been noticed in diffusion measurements with small molecules¹⁵ and in measurements of local proton diffusion.¹⁶ It would seem, therefore, that the macroscopic rigidity which occurs at the gel point has little effect on ion motion as the local environment is sufficiently fluid to effectively retain the transport properties of the sol. During aging, conductivity depends on the presence of protons in the solvent phase. Recent experiments have shown that the use of solvent exchange methods to "wash" the gel removes protons and greatly decreases the conductivity of the aged gel.¹⁷ These experiments demonstrate that as long as the solvent phase remains continuous, it can dominate the proton transport behavior. Finally, drying of the gel produces a high resistivity material once the water layer either becomes discontinuous or vanishes altogether.

There have been several studies in which sol-gel derived approaches lead to materials with either high proton or lithium ion conductivity within the structure. One interesting method involves the synthesis of an inorganic-organic material as alkylamines were used as network modifiers to prepare "aminosils" via the hydrolysis of a mixture of aminated organosiloxanes $(\text{R}'\text{Si}(\text{OR})_3)$ ($\text{R} = \text{amino group}$; $\text{R}' = -\text{CH}_3$ or $-\text{C}_2\text{H}_5$) and an acid.¹⁸ The silica backbone provides mechanical strength while organic amino groups offer solvating properties with respect to the guest ionic species. Films of the material were transparent and exhibited proton conductivity in the range 10^{-5} S/cm at room

temperature. Another organic modified approach has involved titanium oxides. In general, organic modification of transition metal oxide gels is difficult because the more polar M—C bond would be broken upon hydrolysis. However, a rubbery material in which Ti—O—Ti polymeric species are linked through organic bridges was prepared by hydrolyzing Ti(OR)_4 in the presence of glycerol and acetic acid.¹⁹ The proton conductivity of these materials varies with the amount of acetic acid and values in the range of 10^{-5} S/cm at room temperature were reported. It is interesting to note that adding LiClO_4 to the gel produced higher conductivities (10^{-4} S/cm) with the titanium oxide materials.¹⁹ The addition of lithium salts to organically modified silicates has also been reported.²⁰ The synthesis of these materials involved mixing polyethylene glycol and silicon alkoxides and adding lithium salts dissolved in the same solvent as that of the base solution. The resulting conductivity was about 10^4 times greater than that of the undoped gels and values of nearly 1×10^{-4} S/cm were obtained at room temperature. These lithium salt containing materials represent the sol-gel analogs of polymer electrolytes.

Proton conduction in other oxide systems has also been studied. The transition metal oxide gel, $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, has received considerable interest.²¹ These gels are mixed electronic-ionic conductors with ionic conduction from proton diffusion dominating for $n > 0.5$. The material contains water molecules trapped in a layered oxide network and the observed electrical properties depend on the oxide and liquid phases and the corresponding interface. The presence of water is also instrumental in producing a wide range of intercalation reactions. Specific diffusion mechanisms are related to the number of water molecules in the interlamellar spacing. Below $n = 0.5$, the water molecules trapped within the oxide network cannot diffuse through the structure and are too far apart to enable protons to jump from site to site. The ionic conductivity increases as more water molecules are intercalated within the layer. At $n = 1.8$, when the first monolayer is intercalated, proton diffusion occurs through an ordered array of hydrogen bonded water molecules and conductivity reaches 10^{-2} S/cm. For $n > 1.8$, proton conduction becomes similar to that of an acid aqueous solution.²¹

4. ELECTRODE MATERIALS

There have been a significant number of studies regarding the potential use of transition metal oxide gels as reversible cathodes in lithium batteries. Gel materials have been investigated as part of the general interest in reversible

intercalation of Li^+ in two dimensional host lattices. The transition metal oxide gels are mixed conductors. The proton conduction properties were discussed above and the ability of these materials to support Li^+ conduction is well established for systems such as V_2O_5 , WO_3 and MnO_2 among others. Electronic conduction through the oxide network arises from electron hopping between metal ions in different valence states. The behavior of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels and xerogels has received the most study not only because of the straight forward synthesis of the materials, but also because of the high redox potential for V_2O_5 .

In the paragraphs below we discuss three areas involving sol-gel derived electrode materials. In the first case, the importance of morphological considerations is presented. The second area concerns the use of sol-gel methods to prepare novel inorganic-organic electrodes. Finally, we present the prospects for using aerogels as electrochemical materials.

The electrochemical behavior of the vanadate gels has been studied by several groups, however, relatively little attention has been given to issues of film chemistry and morphology at the nanometer level. Just as the local chemical environment is found to be instrumental in controlling proton conduction, similar considerations of local chemistry and structure are expected to be important factors in determining electrochemical properties. TEM studies have shown that $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels form ribbon-like fibers. There have yet to be studies, however, of how these entities pack and arrange themselves in films. The evidence from x-ray diffraction suggests that the ribbons exhibit some form of preferred stacking with characteristic two-dimensional ordering.²³

We have begun to use atomic force microscopy (AFM) to characterize the morphology of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels as a function of film processing. Fig. 2 shows a dip coated film prepared using the decavanadic acid approach. The film has a morphology consisting of a complex folding of the aggregates which are present in the gel phase. The aggregates themselves consist of the ribbon-like colloids observed by TEM. The AFM image clearly suggests that the morphology of the coating is determined by the aggregation occurring in the gel-state as the aggregates dry upon each other forming a lamellar texture throughout the coating.

By diluting the gel it is possible to obtain better resolution of the individual aggregates. An AFM image of a film formed by diluting the decavanadic acid solution by a factor of five is shown in Fig. 3. The image indicates that there is less aggregation in this film and that it is now possible to

observe individual aggregates. This type of morphology is expected to be representative of the corresponding sol.

In future work it will be extremely interesting to determine how the morphology is influenced by intercalation processes. With the use of AFM, it will be possible to study the changes occurring within the aggregates as well as between the aggregates. The ability to use AFM to characterize the individual micro-aggregates is shown in Fig. 4 which was also obtained by diluting the decavandic acid solution by a factor of five. The individual micro-aggregates are of average dimension $3\text{ }\mu\text{m}$ long by $1000\text{ }\text{\AA}$ wide by $50\text{ }\text{\AA}$ high. Using AFM it will be possible to quantify the dimensional changes which occur in these micro-aggregates upon intercalation and de-intercalation reactions.

Another interesting electrode material that exploits sol-gel synthesis is an inorganic-organic system which involves the use of conducting polymers. Rather than attaching the organic constituent, Kanatzidis et. al. used intercalation/polymerization of organic monomers in the interlamellar space of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels.¹⁰ This work takes advantage of the ability of vanadate xerogels to intercalate a wide variety of inorganic and organic guest species including monomers such as aniline, pyrrole and 2,2'-bithiophene. The organic monomers are oxidatively polymerized into electrically conductive polymers contained within the layer. These molecular-level composites exhibit higher conductivity than that of the inorganic component and, by inserting the polymer within the interlamellar spaces, there is the prospect of achieving oriented polymers.

In recent work we have synthesized V_2O_5 /polyaniline materials and begun to investigate their electrochemical properties. The resulting materials possess higher conductivity than the V_2O_5 xerogels and flexible, self-supporting films have been prepared. Cyclic voltammetry results from our initial samples (shown in Fig. 5) clearly indicate the electrochemical intercalation and de-intercalation of lithium. This behavior is somewhat different than that of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ films which exhibit far broader peaks under comparable cycling conditions.

The use of conducting polymers in an inorganic-organic electrode material appears to have considerable potential. The resulting composite will, ideally, possess the best features of each constituent. The electronic conductivity will be larger than that of the $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels and the mechanical integrity will be greatly improved. In this configuration where the polymer is in the interlamellar space, it is accessible to the redox reactions in V_2O_5 and there is the opportunity

to oxidize and reduce the polyaniline via the oxide network. In this way it may be possible to intercalate lithium into both the inorganic and organic constituents and there will be little loss of capacity from adding the conductive component. Another interesting feature with these materials is that by filling the interlamellar space, the problems associated with the intercalation of organic solvents such as propylene carbonate will be avoided.²³ Finally, it should be mentioned that by using appropriate monomers, *in-situ* electrochemical polymerization can be obtained.

A third type of sol-gel derived material which may be of considerable interest for electrode materials is that of transition metal oxide aerogels. Aerogels are sol-gel derived materials with porosities from about 80% to over 99% (in contrast, xerogels are in the range of 50%). The high porosity is achieved by the supercritical drying (SCD) of a wet (or aged) gel.²⁴ In this way it is possible to produce solid materials whose volume is comparable to that of the sol. Typical aerogels will have a solid content of < 1%, a density in the range of 0.3 to 0.03 g/cc and surface areas of close to 1000 m²/g. An extremely important consideration for electrochemical applications is that 90% of the pore volume in these highly porous aerogels is from pores with diameters between 60 and 200 nm.²

The electrochemical properties of aerogels have not been reported, however, these materials are likely to possess interesting properties. The electrochemical reactions which occur with these high surface area materials will be dominated by the properties of surfaces and interfaces - and not the bulk. Since the solid phase of aerogels consists of 3-5 nm particles linked into a three-dimensional network, the electrochemistry that occurs in the solid phase is truly nanodimensional.

We have prepared vanadate aerogels using VO(OC₂H₅)₃ in ethanolic solutions. After aging for one week at 60°C, the gels were dried supercritically for two hours at a pressure of 200 atm. and a temperature of 250°C. The resulting materials are amorphous and very light weight (\approx 0.2 g/cc). Initially the samples were black in color, however, upon ambient exposure they became green. This coloration effect has been frequently observed in vanadate gels and is attributed to some reduction of the vanadium ions.²¹ The mixed valence occurring in the material suggests that these materials will be electronically conducting. The microstructural and electrical properties of these vanadate aerogels are under investigation.

5. SUMMARY AND CONCLUSIONS

It appears that sol-gel chemistry has a great many potential applications in the preparation of new and unusual electrodes and electrolytes; from non-equilibrium transition metal oxides which may be of use as high energy density electrodes to high surface area oxides which should exhibit high proton conductivity to novel composite structures of inorganic gels and organic electronic and ionic conductors. To date, very few aspects of the electrochemistry of sol-gel derived materials have been investigated.

The sol-gel route should make it possible to create both new materials and materials in which new phenomena are observed. Examples of new materials include the inorganic-organic composite materials and transition metal oxide aerogels. The latter represent an example of where new phenomena may be exploited. The high surface areas and short diffusion paths in the solid phase of these materials may enable intercalation reactions to occur at rather high rates; in conventional materials with the usual bulk dimensions, the intercalation reactions might occur far too slowly to be of interest. Alternatively, surface conduction processes that would represent minor contributions in a dense sample will dominate the characteristics of the high surface aerogels when water is adsorbed.

Finally, it is important to mention that the still very new technique of atomic force microscopy is well suited for examining the evolution of surface structure during electrochemical and chemical reactions. This paper presents some of the first AFM images of a gel and it is already evident that the technique offers new insights concerning gel structure and its transformations. Future work using AFM should prove very useful in understanding the nature of the electrochemical redox reactions and the active redox centers in gels.

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FIGURE CAPTIONS

Figure 1. Bulk resistance of acid catalyzed silica gel before and after gelation.¹⁴

Figure 2. AFM image of a vanadate film showing the morphology of the collapsed gel. The film is $\approx 3\mu\text{m}$ thick. The highest feature in the image is 300 nm.

Figure 3. AFM image of a vanadate film prepared using a diluted sol.

Figure 4. AFM image of micro-aggregates of vanadium oxide gel prepared by the decavanadic acid method. Average dimensions of the micro-aggregates are $3\mu\text{m}$ length by 1000 \AA width by 50 \AA height.

Figure 5. Cyclic voltammetry of the system:

Li/LiClO₄ in propylene carbonate/Vanadium oxide-polyaniline/Pt

The potential is referenced to lithium. The open circuit voltage for the cell is $\approx 3.1\text{ V}$.

The oxidation and reduction peaks become enhanced with cycling (scan rate: 1mV/s). The third scan through the eighth scan is shown.

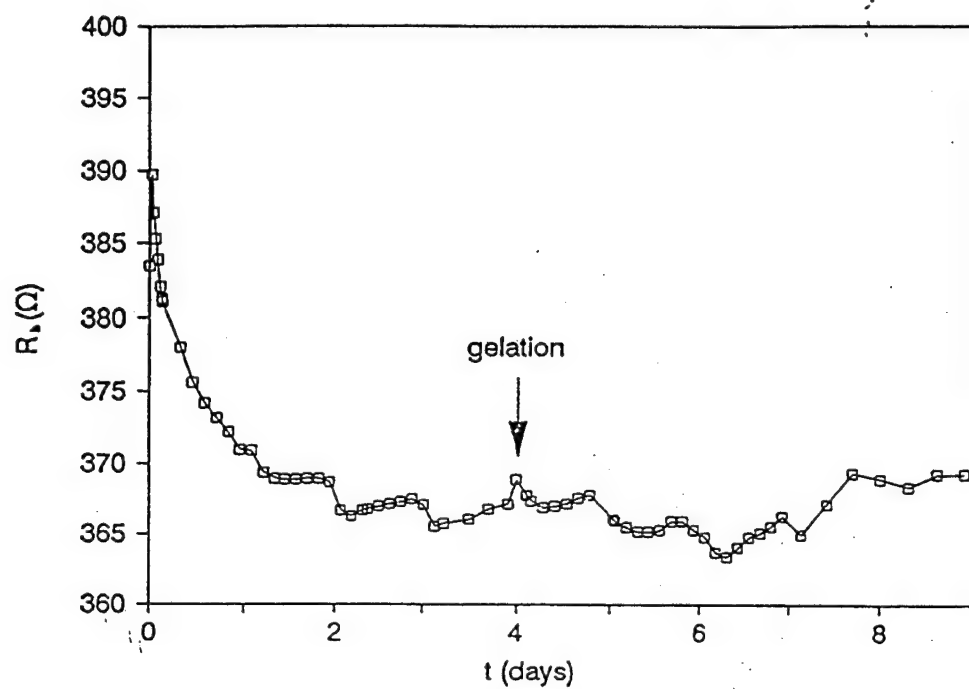


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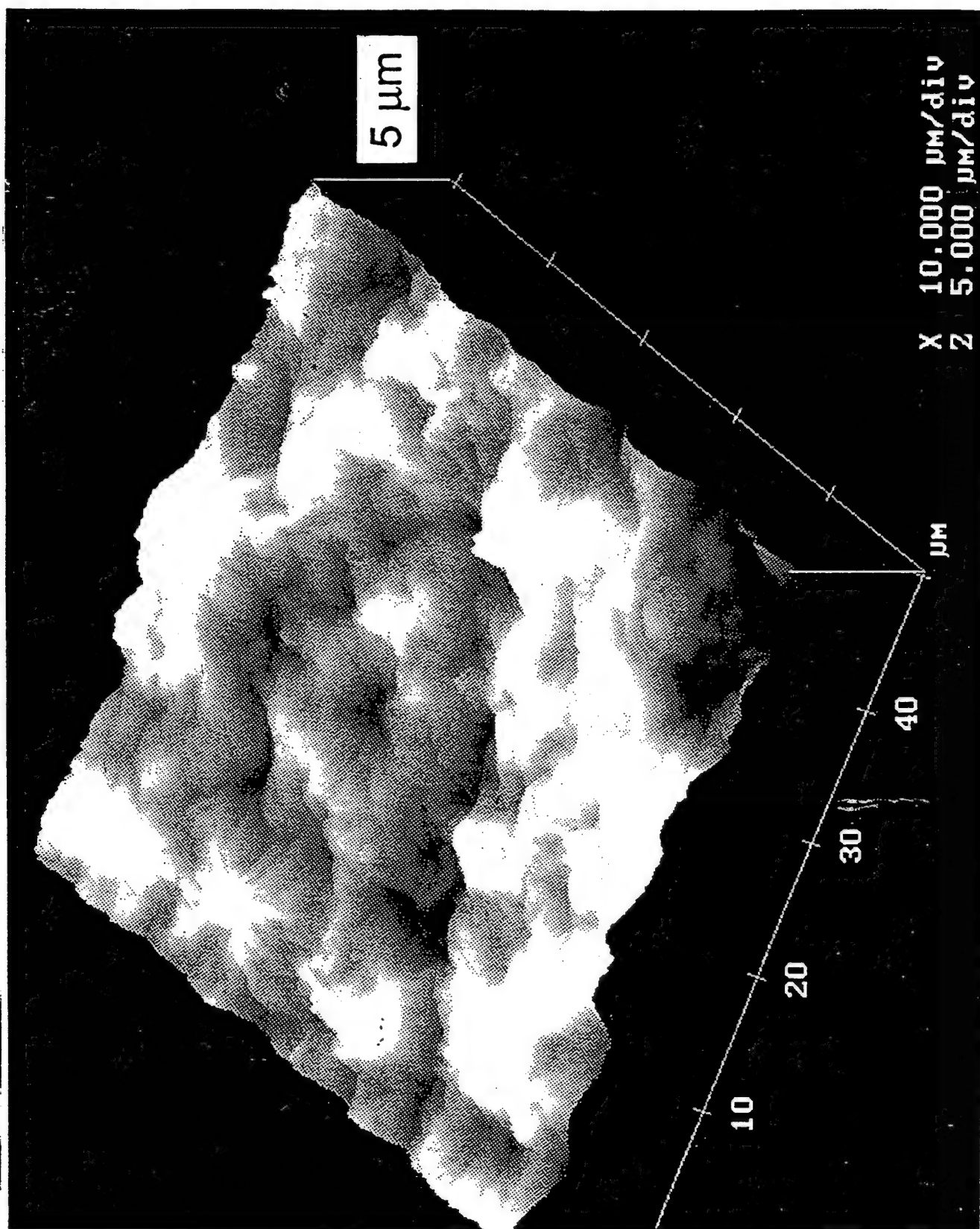


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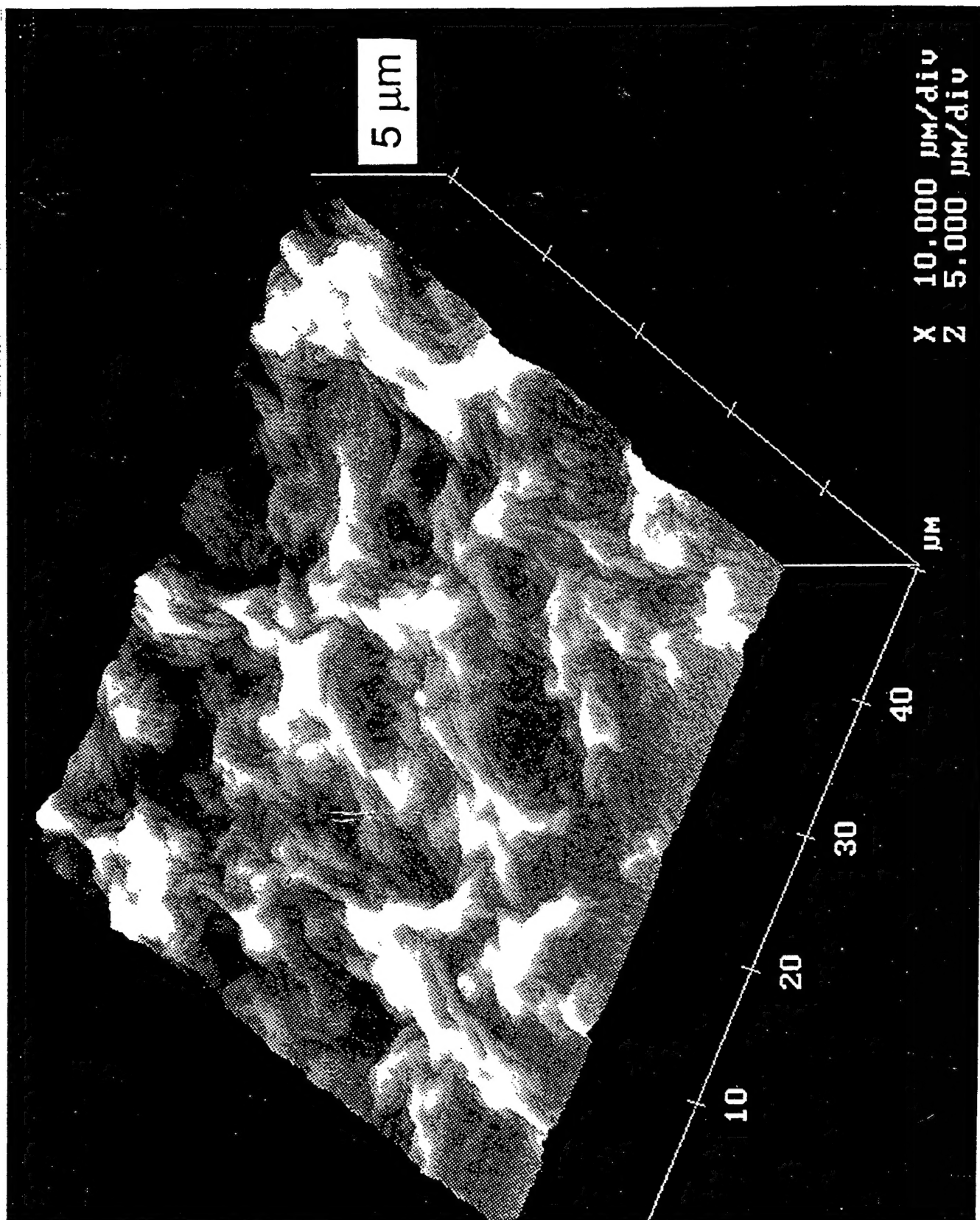


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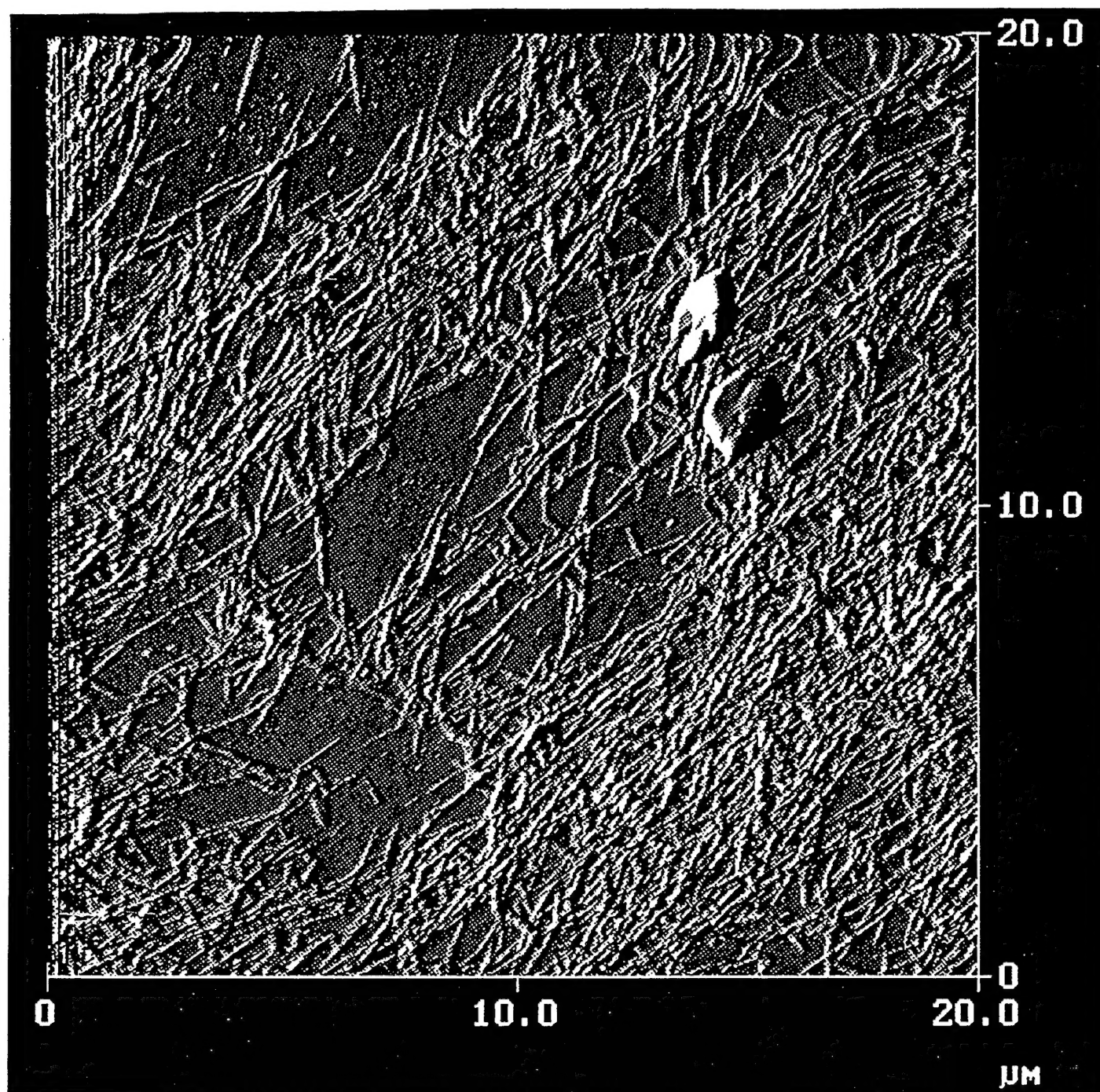


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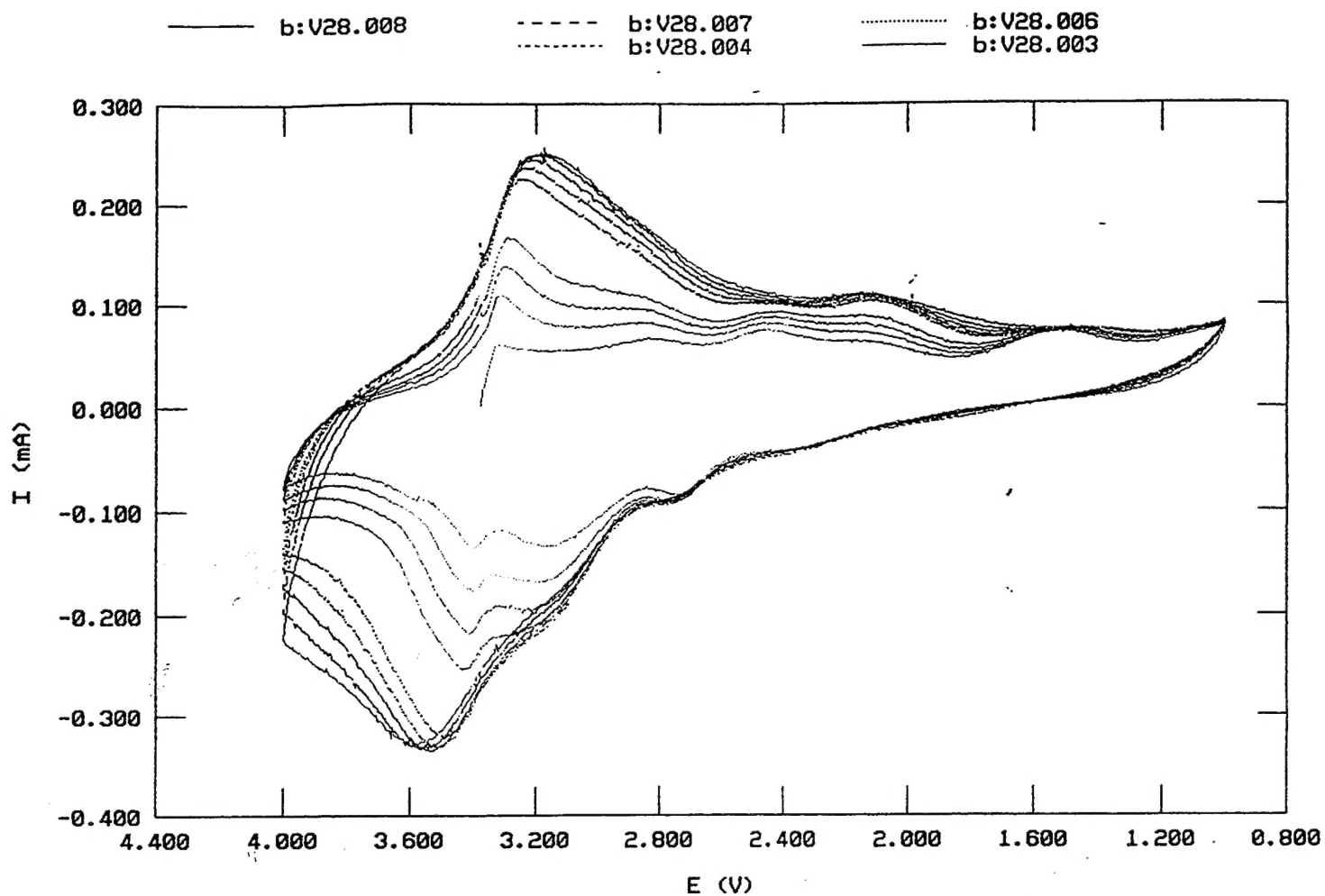


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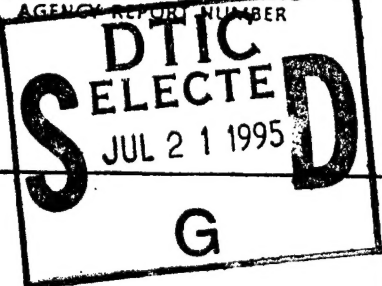
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